SYNTHESIS OF Pb(II) IMPRINTED CARBOXYMETHYL CHITOSAN AND THE APPLICATION AS SORBENT FOR Pb(II) ION

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ABSTRACT

The aims of this research is to synthesize Pb(II) imprinted polymers with carboxymethyl chitosan (CMC) as polymers and bisphenol A diglycidyl ether (BADGE) as cross-linker (Pb-IIP). Chitosan (CTS), non imprinted polymer (NIP) and Pb-IIP were characterized using infrared (IR) spectroscopy, X-ray diffraction (XRD), surface area analyzer (SAA), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) spectroscopy. The result showed that the adsorption was optimum at pH 5 and contact time of 250 min. Adsorption of Pb(II) ion with all of adsorbents followed pseudo-second order kinetic equation. Adsorption of Pb(II) ion on CTS followed Freundlich isotherm while that on NIP and Pb-IIP followed the Langmuir adsorption isotherm. The adsorbent of Pb-IIP give higher capacity than the NIP and CTS. Adsorption capacity of Pb-IIP, NIP and CTS were 167.1, 128.9 and 76.1 mg/g, respectively. NIP gave higher adsorption selectivity for Pb(II)/Ni(II) and Pb(II)/Cu(II), whereas Pb-IIP showed higher adsorption selectivity for Pb(II)/Cd(II).The hydrogen bonding dominated interaction between Pb(II) ion on NIP and Pb-IIP.

Keywords: *ion imprinted polymers; carboxymethyl chitosan; BADGE; adsorption; Pb(II) ion*

ABSTRAK

Tujuan penelitian ini adalah mensintesis material imprinting ion Pb(II) pada karboksimetil kitosan dengan kroslingker bisfenol A diglisidil eter (BADGE) (Pb-IIP). Kitosan (CTS), non imprinting polimer (NIP), dan Pb-IIP dikarakterisasi dengan spektrofotometer FTIR, difraksi sinar-X (XRD), analisis luas permukaan (SAA), mikroskop elektron (SEM) dan dispersif energi sinar-X (EDX). Hasil penelitian menunjukkan bahwa adsorpsi ion Pb(II) optimum pada pH 5 dan waktu kontak 250 menit. Adsorpsi ion Pb(II) pada semua adsorben mengikuti persamaan kinetika pseudo orde-dua. Adsorpsi ion Pb(II) pada CTS mengikuti isoterm adsorpsi Freundlich sedangkan pada NIP dan Pb-IIP mengikuti isoterm adsorpsi Langmuir. Pb-IIP mempunyai kapasitas adsorpsi paling tinggi dibandingkan NIP dan CTS. Kapasitas adsorpsi ion Pb(II) pada Pb-IIP, NIP dan CTS masing-masing sebesar 167,1; 128,9 dan 76,1 mg/g. NIP memberikan selektivitas adsorpsi terbesar untuk Pb(II)/Ni(II) dan Pb(II)/Cu(II), sedangkan Pb-IIP memberikan selekivitas adsorpsi terbesar untuk Pb(II)/Cd(II). Interaksi Pb(II) pada Pb-IIP dan NIP didominasi oleh ikatan hidrogen

Kata Kunci: *polimer tercetak ion; karboksimetil kitosan; BADGE; adsorpsi; Pb(II)*

INTRODUCTION

Metal ions were released into the environment by many industries through their waste water. Some of metal ions are toxic elements for living organism especially human, therefore their removal from waste water is important [1-3]. Lead (Pb(II)) is attracting wide attention of environmentalist as one of the most toxic heavy metals. The major sources of Pb(II) are industries of the smelting of iron and steel, battery, the metal coating, paint, color/textile, and electrical wiring [4-6]. Current treatments to remove metal ions from contaminated water are mostly based on ion-exchange, reversed osmosis, liquid extraction, electrolysis, adsorption, complexation, and precipitation. Among the methods, adsorption is a process which gets increasingly attention because it is generally simple, inexpensive, and able to reduce metal ions until a very low concentration [2,4].

Chitosan is the deacetylation product of chitin, a biopolymer that is contained in the exoskeleton of shrimp, crustacea and insect. Chitosan has biological and chemical properties such as biocompatibility, non-toxicity, high chemical reactivity, chelation and

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adsorption [7-8]. Chitosan has high sorption capacity for several metal ions because it possess a number of functional groups such as hydroxyl and amine groups that can bind metal ions by chemisorption and physisorption [9-10]. Chitosan has several disadvantages when used directly as an adsorbent such as its dissolve in acidic solution, prone to swelling, weak mechanical stability and small adsorption capacity for certain metal ions [4]. Chitosan can be modified by cross-linking [6], immobilizing into a matrix support [11] and blending [12] to make chitosan that stable in acid and has good mechanical properties. The cross-linking procedure may be performed by reaction of chitosan with different reagent such as epichlorhydrin (ECH) [13] glutaraldehyde (GLA) [14-15] and EGDE (16-18]. Though cross-linking reduces the adsorption capacity, but it will increase the stability of the polymer [12].

Molecular imprinting technology (MIP) is a technique to produce polymer materials with specific template by inserting template molecule, cross-linking and removing molecule from the polymer target. Ion imprinted polymers (IIP) are similar to MIP, but instead of a molecule, an ion is used as the template. So that they recognize givens ion after imprinting [19-20]. Ionic imprinted adsorbent based on chitosan have been prepared as an effective adsorbent for Ag(I) [21], Co(II) [22], Pb(II) [23] and As(II) [24].

In this research, a new type Pb(II) ion imprinted adsorbent was synthesized and applied as Pb(II) ion sorbent. The sorbent was prepared by sorption of Pb(II) on carboxymethyl chitosan (CMC) followed by cross-linking using bisphenol A diglycidyl ether (BADGE), and then the sorbed Pb(II) was released using acidic solution. Pb(II) imprinted polymers obtained in this research was then used as adsorbent of Pb(II) ion. The preparation process of materials and adsorption properties were studied in this research.

EXPERIMENTAL SECTION

Materials

Chitosan with the deacetylation degree in the range of 75–85% and bisphenol A diglycidyl ether (BADGE) were purchased from Sigma Aldrich (Germany). Chloroacetic acid, n-propanol, sodium hydroxyde pellet, HCl 37%, fumed HNO_3, $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Ni(NO_3)_2$, Na_2EDTA, and KNO_3 were purchased from E. Merck (Germany). Double distillate water was obtained from Chemistry Laboratories UGM.

Instrumentation

Instruments used in this study were pH meter (TOA HM-30R), Shaker (Marus Instrumenten), Oven (Heraeus), AAS (Perkin Elmer 3110), analytical balance (Mettler Toledo AB54-S), FTIR Spectrophotometer (Shimadzu 8201PC), XRD (Shimadzu XRD-6000) and SEM-EDX (JSM 6360 LA), SAA (Quantachrome Nova 1200e).

Procedure

Preparation of adsorbent

Chitosan (4.0 g) was dispersed in 80 mL isopropanol and stirred for 30 min. NaOH 40% (25 mL) was then added dropwise for 30 min and followed by dropwise addition of 125 mL chloroacetic acid in isopropanol (0.2 M). The reaction mixture was stirred at room temperature for 20 h. The reaction product was filtered, extensively washed with ethanol and then dried in the oven at 100 °C for 24 h. The product was as CMC characterized using FTIR.

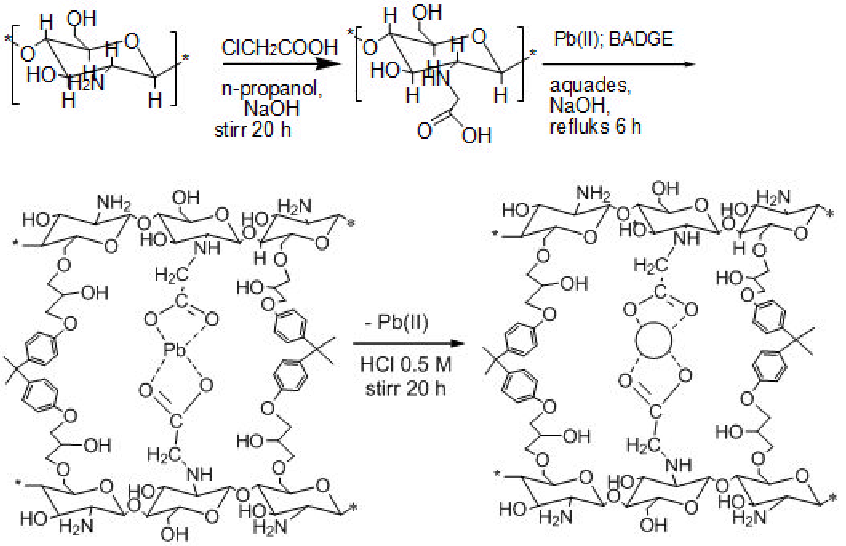
The CMC produced from the previous step was added to a 450 mL beaker flask containing Pb(II) 0.02 M at pH 5, and stirred for 20 h to adsorp Pb(II) ion. The product was filtered and washed with distilled water until no Pb(II) ion in the filtrate was detected using Na_2S solution. The product as CMC-Pb was characterized using FTIR.

The obtained CMC-Pb was put in a round flask containing 150 mL of distilled water, 5 mL of 1 M NaOH and 4.029 g BADGE. The mixture was refluxed for 6 h. The product was filtered and washed by ethanol and distilled water until the pH is neutral. The product as CMC-Pb-BADGE was characterized using FTIR and SEM-EDX.

CMC-Pb-BADGE was dispersed into 500 mL HCl 1 M and stirred for 20 h. The product was filtered and the process was repeated until Pb(II) was undetectable in the filtrate. The product was washed with aquadest and dried in the oven at 110 °C for 24 h. For comparison, the non imprinted polymers (NIP) was also synthesized by direct BADGE cross-linking into CMC. The final products (Pb-IIP and NIP) were characterized using FTIR, XRD, SEM-EDX, and SAA.

Adsorption experiment

The adsorption experiment was performed using bath method at pH 2.0 to 6.0. The intended pH was adjusted using HNO_3 and NaOH. Adsorbent (15.0 mg) was done with 25.0 mL Pb(II) (150 mg/L) solution for 20 h at 40 rpm. The mixture was filtered by Whatman filter paper No. 42, and concentration of Pb(II) in filtrate was analyzed using Atomic absorption spectrometer (AAS). Variation of contact times (0 to 1500 min) was used for determination of adsorption kinetics. Similar work was carried out by varying the concentration of Pb(II) (0 to 500 mg/L) for the determination of adsorption isotherm. Adsorption selectivity was



Scheme 1. Scheme of syntheses Pb(II) imprinted polymer (II) (Pb-IIP)

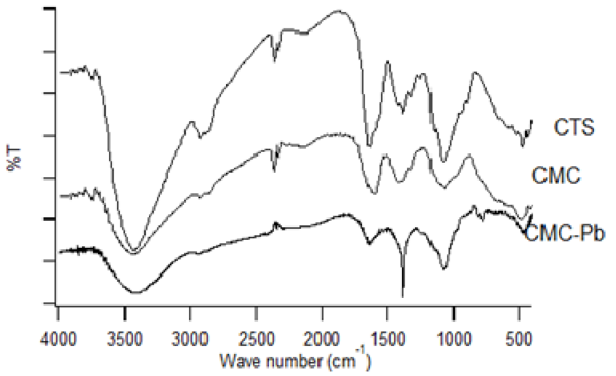


Fig 1. FTIR spectra of CTS, CMC and CMC-Pb

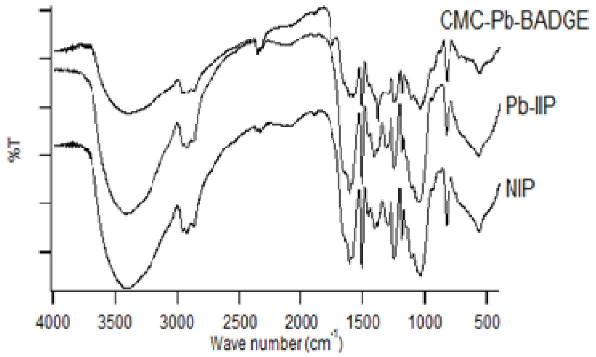


Fig 2. FTIR spectra of CMC-Pb-BADGE, Pb-IIP and NIP

evaluated based on the data of binary competitive metal ions adsorption for Pb(II)/Cu((II), Pb(II)/Cd(II) and Pb(II)/Ni(II). Type of interaction between Pb(II) and the adsorbent was elucidated by performing sequential desorption of adsorbed Pb(II) in water, KNO_3 (0.1 M), HNO_3 (0.1 M) and 0.1 M Na_2EDTA, respectively [25].

RESULT AND DISCUSSION

Characterization Materials

Pb-IIP was synthesized through 4 reaction stages (Scheme 1), namely: 1) grafting of chloroacetic on chitosan (CMC), 2) adsorption of Pb(II) ion on CMC (CMC-Pb), 3) Cross-linking CMC-Pb using BADGE (CMC-Pb-BADGE), and 4) release of Pb(II) ion from CMC-Pb-BADGE (Pb-IIP).

Infrared spectra of CTS, CTS-Pb, CTS-Pb-BADGE, Pb-IIP dan NIP were shown in Fig. 2 and 3. Fig. 2 showed peaks at 3335 cm^{-1} assigned to the stretching vibration of -OH and –NH groups. The peak at 2868 cm^{-1} is due to –CH stretching vibration of –CH and CH_2. The peak at 1635 cm^{-1} is characteristic vibration of C=O from amide, that is overlap with NH vibration from amine groups at 1592 cm^{-1}. The spectrum of CMC showed adsorption peaks at 3335 cm^{-1} which is widened and weakened. The characteristic absorption bands of the asymmetric and symmetric stretching vibrations of COO^- (1600 and 1412 cm^{-1}) were observed in the spectrum of CMC [26-27]. Adsorption of Pb(II) onto CMC showed the new peak at 1381 cm^{-1} of COO-Pb. The weakening of the peak at 1600 cm^{-1} showed interaction between COO^- with Pb(II) ion.

Fig. 3 showed new peak at 1242 and 1512 that are C=C stretching from aromatic after cross-linked CMC using BADGE. A new peak at 825 cm^{-1} indicated the symmetry and asymmetry stretching vibration of para-substituted benzene [28]. The spectrum of Pb-IIP showed that peak at 1743 and 1381 cm^{-1} is disappeared due to desorption of Pb(II) ion from

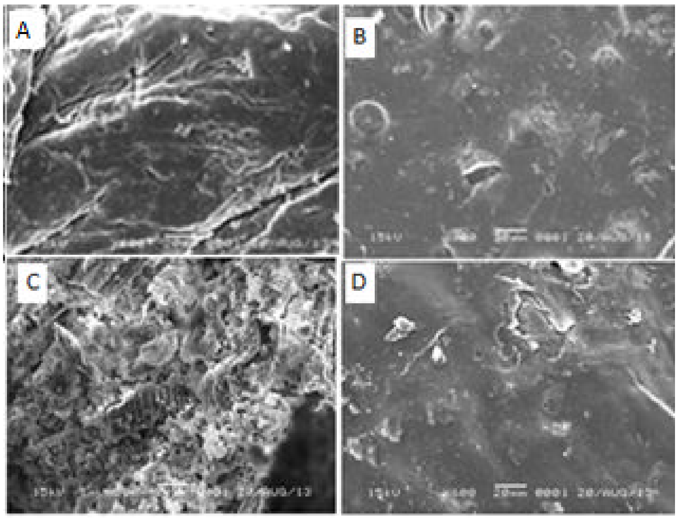


Fig 4. SEM-EDX image of CTS (A), CMC-Pb-BADGE (B), Pb-IIP(C) and NIP(D)

adsorbent. Peak at 1600 cm^{-1} increased due to released Pb(II) from carboxylate groups. Adsorbent NIP showed similar infrared spectrum as Pb-IIP.

The CTS, CTS-Pb-BADGE, Pb-IIP and NIP were characterized using scanning electron microscopy (SEM) (Fig. 4). SEM image of chitosan showed smooth, fibrous a non porous appearance. While on the SEM of CMC-Pb-BADGE showed smoother surface than chitosan. The surface Pb-IIP showed irregular, rough surface due to release of Pb(II) ion from the material. The rough surface of the adsorbent is more beneficial to the homogeneous binding of template ions [28]. SEM image of NIP showed similarity to CMC-Pb-BADGE.

The EDX analysis was performed to identify the elemental composition of CTS, CTS-Pb-BADGE, Pb-IIP and NIP. The data showed that the adsorbed Pb(II) ion in CMC was not released during cross-linking of CMC using BADGE. The elemental percentage of Pb in CMC-Pb-BADGE was 33.74%. Desorption of Pb(II) from Pb-IIP using HCl 1.0 M can release Pb(II) from material and precentage of Pb in Pb-IIP decreased down to 2.02%. This data showed that the imprinting process of Pb(II) into the adsorbent material was succesfully obtained.

Surface area analyzer (SAA) was performed to determine the effect of grafting, cross-linking and imprinting on chitosan toward surface area, pore radius and pore volume. The result of SAA analysis was shown on Table 1. Cross-linking chitosan with and without Pb(II) imprinting decrease the surface area of the material due to the coverage of the surface by cross-linker [29]. The surface area of chitosan, NIP and Pb-IIP were 94.076, 1.397 and 7.451 m^2/g, respectively. The surface area of Pb-IIP was higher than that of NIP due to the imprinting process that produces a new pore resulting from released Pb(II). Pore diameter of Pb-IIP and NIP are higher than chitosan due to grafting of chloroacetic acid and cross-linking give a new pore. In contrary, the grafting and cross-linking process reduce pore volume significantly. It means that, these processes have blocked the small sized pores.

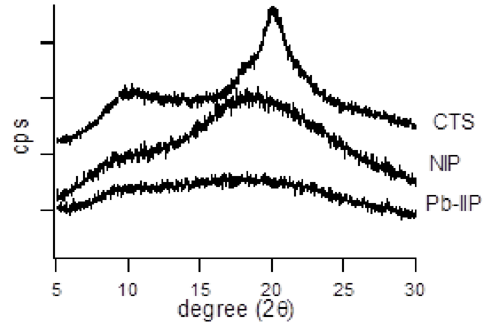


Fig 5. XRD pattern of CTS, NIP and Pb-IIP

Table 1. Surface area, average pore diameter and pore volume of CTS, NIP and Pb-IIP

Adsorbent	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume cc/g x 10^{+3}
CTS	94.076	2.30	110
NIP	1.397	64.26	5
Pb-IIP	7.451	162.80	61

Fig. 5 showed the XRD pattern of CTS, NIP, and Pb-IIP. The XRD pattern of chitosan showed typical peaks at an angle (2θ) of 10° and 20° degrees [30]. Grafting chloroacetic acid and cross-linking on the chitosan (NIP) decreased the crystallinity of chitosan as indicated by the weakening of the peak at 10° and 20° [31]. These peaks shifted toward smaller angle indicated that distance between chitosan chains increased [32]. Pb-IIP showed there are no peak in the XRD pattern due to crystallinity of chitosan was disrupted due to Pb(II) imprinting.

The Effect of pH on Pb(II) Adsorption

The effect of pH on the adsorption of Pb by CTS, NIP and Pb-IIP was studied in the pH range between 2 to 6. As shown in Fig. 6, the adsorption of Pb(II) ion was highly dependent on the pH because pH can affect the solubility of the metal ions and the ionization state of functional groups on the adsorbent. In the lower pH (2-3), adsorption ability of adsorbent is very low since more protons are available and functional groups are protonated. Chitosan has amine (pKa 6.2) and hydroxyl groups as active sites, whereas NIP and Pb-IIP have amine, hydroxyl and carboxylate (pKa 4.6) groups [31,33]. The protonated functional groups exert a repulsive force toward Pb(II), which prevent Pb(II) ion from approaching the adsorbent surface. With the increase of pH value (pH 4-6) made functional group

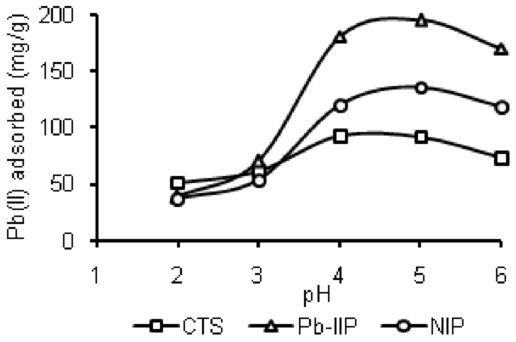


Fig 6. Effect of pH on adsorption capacity of Pb(II) ion by CTS, Pb-IIP and NIP

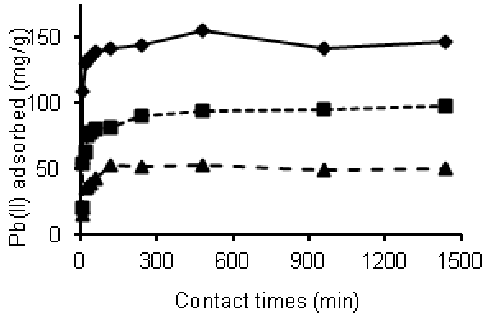


Fig 7. Effect of contact time on adsorption capacity of Pb(II) ion by CTS, Pb-IIP and NIP

Table 2. Kinetic parameter for Pb(II) adsorption onto CTS, NIP and Pb-IIP

Adsorbent	Parameters					
	Pseudo-order 1			Pseudo-order 2		
	q_{e1} (mg/g^{-1})	k_1 (L/min)	R^2	q_{e2} (mg/g^{-1})	k_2 (g/mg min)	R^2
CTS	34.51	0.025	0.901	52.6	0.17	0.998
NIP	39.99	0.012	0.594	100.0	0.09	0.996
Pb-IIP	37.15	0.005	0.520	166.6	0.21	0.999

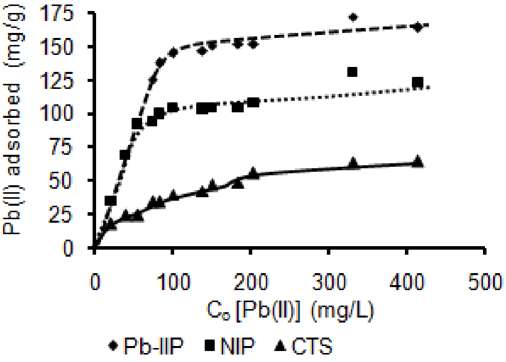


Fig 8. Effect of initial concentration on adsorption capacity of Pb(II) ion by CTS, Pb-IIP and NIP

deprotonated and able to bind metal ions so adsorption ability increase. When pH > 6, precipitation of lead hydroxide start occurring that can't be adsorbed and therefore the adsorption ability decrease [34].

Adsorption Kinetics

The adsorption kinetics of Pb(II) on chitosan, NIP and Pb-IIP were studied at various contact times and at optimum pH 5. The profile of contact time effect on the adsorption of Pb(II) is shown in Fig. 7. Initially, the adsorption Pb(II) (mg Pb(II)/g adsorbent) increased quickly due to most of active sites on the adsorbent were fully empty. Adsorption equilibrium was reached at 250 min, and longer time no change in adsorption was occurred. Two kinetic models are pseudo-first order (Lagergren) and pseudo-second order (Ho) equations were applied on the experimental data to investigate the potential rate-determining step of the adsorption process [35-36].

The linier form of the pseudo-first order equation is given by equation (1) [36]

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (1)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of the first-order adsorption.

Pseudo second order kinetic equations is expressed in equation (2)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

where k_2 (g/mg min) is a pseudo second order constant.

Table 2 showed the parameters of adsorption kinetic for Pb(II) onto CTS, NIP and Pb-IIP. For all adsorbents, the adsorption data have very low correlation coefficient values (R^2) for the plot of $\ln(q_e-q_t)$ vs. t from the pseudo-first order equation. The pseudo-second order equation correlated well with the experimental data, as shown by high R^2 value (R^2>0.99) of the t/q_t vs. t. The main assumption for the pseudo-second order equation is the limiting step may be chemical adsorption involving valent force through sharing or the exchange of electrons between the adsorbent and divalent metal ions [37]. The rate constant (k_2) for Pb-IIP is the highest. The porous structure of Pb-IIP made Pb(II) ion is faster to reach active site and bind on the functional groups of the adsorbent.

Table 3. Parameters of Langmuir and Freundlich isotherm

Adsorbent	Parameters							
	Langmuir					Freundlich		
	b (mg/g)	K (L/mg)	K (L/mmol)	ΔG (KJ/mol)	R^2	n	K_f (mg/g)	R^2
CTS	76.1	3.092	0.015	-20.25	0.987	2.80	8.0	0.989
NIP	128.9	19.610	0.085	-24.90	0.993	10.00	68.4	0.823
Pb-IIP	167.1	68.889	0.333	-28.06	0.998	19.231	121.3	0.864

Adsorption Isotherm

The adsorption isotherm was studied by varying the initial concentration of Pb(II) ion (0 to 500 mg/L) at pH 4. The effect of concentration of Pb(II) ion on the adsorption capacity is shown in Fig. 8. Several models have been published to describe the adsorption isotherms. In this paper Langmuir and Freundlich adsorption isotherms were used to describe the interaction between the solute and the adsorbent.

Freundlich adsorption isotherm equation is an empirical equation that was used for adsorption on heterogeneous surfaces [4]. The linearized form of the Freundlich isotherm equation is:

$$\log m = \log K_f + \frac{1}{n} \log Ce \qquad (3)$$

where m is the number of metal ions adsorbed (mg/g), K_f (L/g) is the adsorption distribution coefficient related to Freundlich adsorption capacity, and n is the Freundlich constants indicating heterogeneity of the surface.

The Langmuir adsorption isotherm equation describes an adsorption occurring on the surface that has a finite number of sites with similar energy levels. This model based on the assumptions that homogeneous adsorption is occurring on a monolayer surface coverage and without net interaction between the adsorbed species. The linearized Langmuir isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{bK} + \frac{1}{b} C_e \qquad (4)$$

where q_e is the amount of adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mg/L), b is the Langmuir adsorption capacity (mg/g), K (L/mg) is the Langmuir adsorption equilibrium constants that can be used to determine the adsorption energy.

Table 3 showed the parameters of Freundlich and Langmuir adsorption isotherm. Based on Table 3, the adsorption of Pb(II) using the chitosan shows a better fit to the Freundlich due to its high R^2 value (R^2>0.98). On the other hand, the adsorption using NIP and Pb-IIP shows a better fit to the Langmuir isotherm adsorption model (R^2 > 0.99). This fact indicates that grafting and cross-linking onto chitosan produce a homogen active sites on the surface that may be dominated by carboxylate groups.

From the Langmuir isotherm model, it can be recalculated that the adsorption capacity (b) of Pb-IIP was the higest. Adsorption capacity of chitosan, NIP and Pb-IIP were 76.1, 128.9 and 167.1 mg/g, respectively. Grafting of chloroacetic acid onto chitosan enriched the active site of adsorbent. Carboxylate groups on the NIP and Pb-IIP were able to bind Pb(II) ion. Cross-linker BADGE has two benzene rings in their structure, that can bind metal ions by π bonding. Combination of chloroacetic acid grafting and cross-linking increased the adsorption capacity of NIP and Pb-IIP than that of chitosan. Imprinting technique creates more pores on the Pb-IIP, and these pores facilitate more Pb(II) ion to be bound by active sites in the adsorbent. Imprinting processed produced adsorbent material that have high adsorption capacity.

Adsorption energy equation could be written as

$$E_{ads} = - \Delta G° = RT \ln K \qquad (5)$$

where R is the general gas constant (8.314 J/K mole), T (K) is the temperature, and ΔG° is Gibbs energy.

Free energy for physisorption is generally lower than -20 kJ/mol, the physisorption together with chemisorption is at the range of -20 to -80 kJ/mol and chemisorption is at range -80 to -400 kJ mol^{-1} [4]. In Table 3, ΔG° value for adsorption Pb(II) ion on chitosan, NIP and Pb-IIP are -20.2, -24.9 and -28.1 kJ/mol, respectively. Thus the adsorption of Pb(II) onto chitosan, NP and Pb-IIP involve physisorption and chemisorption simultaneously. This fact also shows that the imprinting process increase the strength of the interaction between Pb(II) and the adsorbent.

Adsorption Selectivity

The adsorption selectivities were determined by adding 15.0 mg adsorbent to 25.0 mL of solution containing ion pairs: Pb(II)/Ni(II), Pb(II)/Cu(II), and Pb(II)/Cd(II), with each ion concentration of 0.5 mmol/L. The adsorption was carried out in batch system using magnetic stirrer at pH 5. Selectivity coefficient (α) was determined using equation 7 [26].

$$\alpha_{(M1/M2)} = D_{M1}/D_{M2} \qquad (6)$$

where distribution ratio D = Q/C_e, Q is adsorption capacity (mmol/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mmol/L), and α is selectivity coefficient.

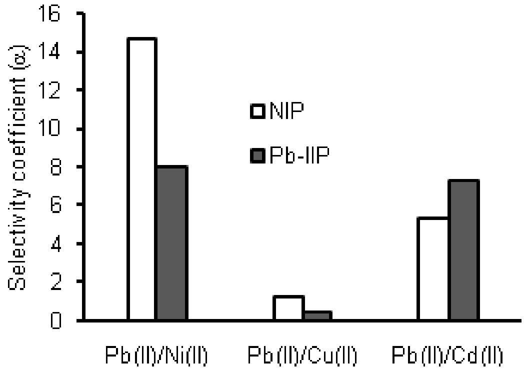


Fig 9. Coefficient selectivity of Pb(II) on NIP and Pb-IIP

Fig. 9 shows selectivity coefficient (α) Pb(II) toward Ni(II), Cu(II) and Ni(II). Adsorption selectivity is influenced by metal ion sizes, properties of metal ions and functional groups. Based on the hard and soft acid and bases principle (HSAB) by Pearson, carboxylate and amine groups are hard base, whereas Pb(II), Cu(II) and Ni(II) are intermediate acid whereas Cd(II) is soft acid [37]. Pb(II) imprinted polymers created pores that appropriate to the size of Pb(II) hydrated ion. Pb(II) hydrated ion has bigger ionic radii than hydrated Cu(II), Ni(II) and Cd(II) ions The ionic radii of hydrated Pb(II), Cu(II), Ni(II) and Cd(II) are 2.74, 2.07, 2.06 and 2.28 Å, respectively [38]. The metal hydrated ion smaller than hydrated Pb(II) ion can enter to this hole and be adsorbed on the adsorbent. The size of Ni(II) and Cu(II) are much smaller than Pb(II) size so these metal ions can be adsorbed on Pb-IIP, selectivity of Pb-IIP for Pb(II)/Ni(II) and Pb(II)/Cu(II) smaller than NIP. Pb-IIP is more selective for Pb(II)/Cd(II) because the size of Cd(II) is relatively big and Cd(II) is soft acid so it is not suitable with active site of the adsorbent.

Adsorption Mechanism

Sequential desorption using water, KNO_3 0.1 M, HNO_3 0.1 M and Na_2EDTA 0.1 M was employed to the study interaction type between Pb(II) ion with adsorbent. The results of desorption process are shown in Fig. 10. This data shows that interaction between Pb(II) ion on NIP and Pb-IIP is dominated by hydrogen bonding. Pb(II) ion in water forms hydroxo complexes, and hydrogen bonding occurs between water bound to Pb(II) and active functional groups (carboxylate and amine) the adsorbent [40]. Entrapment mechanism of Pb(II) ion on Pb-IIP is higher than NIP due to the fact that Pb-IIP is more porous than that of NIP, so that it can entrap more Pb(II) ion. In addition complexation interaction can proceed between Pb(II) ion with amine groups, hydroxyl groups or carboxylate simultaneously.

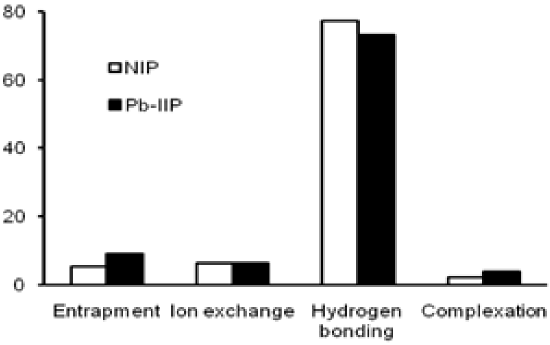


Fig 10. Interaction type of adsorption Pb(II) by CTS, NIP and Pb-IIP

CONCLUSION

In this work, Pb-IIP was prepared using Pb(II) as the imprinted ion, CMC as a polymers and BADGE as a cross-linker. The adsorption capacity of Pb(II) ion on Pb-IIP is the higer than that on NIP and chitosan. The adsorption process could be the best described with pseudo-second order kinetic model and Langmuir adsorption isotherm. Imprinting created new pore that can increase adsorption capacity for metal ions. The interaction between Pb(II) and Pb-IIP was dominantly by hydrogen bonding. The imprinted adsorbent has a good potential for the treatment of industrial waste waters contaminated with heavy metal ions.

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